PRODUCTION OF METHANE FROM PALM OIL MILL EFFLUENT BY USING ULTRASONICATED MEMBRANE ANAEROBIC SYSTEM (UMAS)

YAP WAI MUN

Thesis submitted in partial fulfillment of the requirements

for the award of the degree of

Bachelor of Chemical Engineering (Gas Technology)

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

JANUARY 2012

ABSTRACT

The direct discharge of the Palm Oil Mill Effluent (POME) wastewater causes serious environmental pollution due to its high chemical oxygen demand (COD), total suspended solids (TSS) and biological oxygen demand (BOD). The conventional ways for POME wastewater treatment have both economical and environmental disadvantages. In this study, the potential of ultrasonic-assisted membrane anaerobic system (UMAS) was evaluated as alternative and cost effective method for treating POME wastewater to avoid fouling. Throughout the experiment, the removal efficiency of COD was 95% with HRT of 6 days. The BOD removal efficiency was 74% while TSS removal rate was from 91 to 99.5%.The methane gas production efficiency was 82.14%.The UMAS treatment efficiency was greatly improved by UMAS introduction. The membrane fouling and polarization at the membrane surface was significantly reduced.

Key words: UMAS, Anaerobic,POME,COD,membrane,Ultrasonic

ABSTRAK

Pelepasan air pemprosesan kelapa sawit (POME) tanpa rawatan akan menyebabkan pencermaran kerana ia mengandungi keperluan oksigen kimia (COD), keperluan oksigen biologi (BOD) dan jumlah pejal (TSS) yang tinggi. Rawatan konventional bukan sahaja memerlukan kos yang tinggi juga menyebabkan pencermaran. Dalam kajian ini, potensi kaedah rawatan dengan system membran anaerobik berultrasonik (UMAS) dikaji supaya dijadikan pilihan alternatif dan kaedah kos efektif untuk rawatan air pepmprosesan kelapa sawit dan menggelakkan masalah fouling. Sepanjang kajian ini, didapati bahawa kadar penurunan keperlun oksigen kimia adalah 95% pada hari ke-6.Kadar penurunan keperluan oksigen biologi pula didapati sebanyak 74% manakala kadar penurunan jumlah pejal(TSS) mencatatkan rekod 91% hingga 99.8%.Bacaan tertinggi gas metana yang dihasilkan semasa kajian adalah sebanyak 82.14%.Kecekapan system rawatan UMAS ditingkat dengan ultrasonic yang dipasang. Masalah fouling membrane dan polarisasi didapati berkurangan.

Kata kunci: UMAS,Anaerobik,POME, COD, membran,Ultrasonik

.

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

With the increasing awareness on the environmental issues and the rising of oil price, all governments across the world are forced to looking for alternative energy, the same phenomenon happen in Malaysia as well. The Renewable energy has been recognized as the country's fifth fuel under the 8^{th} and 9^{th} Malaysian Plans. Nowadays, the government claimed to commit to adopting Renewable Energy and Green Technology. The government launched the Green Technology Financing Scheme (GTFS) on 26 Jan 2010 to encourage the effort of looking for alternative energy. The government will play its role, covering two per cent of the loan's interest rate and providing a guarantee of 60 per cent on the financing. The remaining 40 per cent will be covered by banks.

In the 21st century, renewable energy and sustainable energy as well as green technology would be the core of economic growth for all countries. This reflects that Malaysian is in high demand of expertise in Renewable and sustainable energy, hence the project of producing methane gas from palm oil Mill effluent is a high potential project. In addition, Malaysia is the world’s primary palm oil producer. It ranked as the second largest export revenue earner with a total combined value of RM4.5 billion in December 2009. Malaysian palm oil production is expected to reach 18 million tonnes in 2010.Hence, the amount of effluents that produce is escalating, and the waste resources would never be the limitation.

In the process of palm oil milling, Palm Oil Mill Effluent (POME) is produced as a result of sterilization of fresh oil palm fruit bunches, clarification of palm oil and effluent from hydro cyclone operations. POME is a viscous brown liquid which with fine suspended solid and possess high value of COD and BOD. Hence, it is a high strength organic polluter. The discharge of effluent from palm oil mill have been regulated by the Environment Quality (Prescribed Premises) (Crude Palm Oil) Order, 1997 and the Environmental Quality (Prescribe Premises) (Crude Palm Oil) Regulations, 1997 which promulgated under the Environmental Quality Act,1974. In order to reach the requirement of standard discharge limit, waste water treatments can never to be dismissed. It incurs high non-profitable cost in an industry to resolve this problem either the waste water have to be reduced or the treatment have to be enhanced in cost effective way. Instead of the conventional ponding system, the membrane anaerobic system (MAS) will be proposed to be utilized. The system consists of two technology which is anaerobic digestion and membrane separation technology.

The anaerobic digestion is the degradation of complex organic matters under the absence of oxygen. In the process, POME is degraded into methane, carbon dioxide and water. , there is a sequence of reactions involved; hydrolysis, acidogenesis (including acetogenesis) and methanogenesis. Hydrolysis is where complex molecules (i.e., carbohydrates, lipids, proteins) are converted into sugar, amino acid and etc. In the step of acidogenesis, acidogenic bacteria will break down these sugar, fatty acids and amino acids into organic acids which mainly consist of acetic acid (from acetogenesis) together with hydrogen and carbon dioxide. Hydrogen and carbon dioxide will be utilized by hydrogenotropic methanogens while acetic acid and carbon dioxide will be utilized by acetoclastic methanogens to give methane as a final product. Hence, it enables the concept of waste to energy.

With the addition of application of membrane filtration in the system, the efficient of wastewater treatment is elevated that is capable of retaining biomass concentration within the reactor and produce high quality effluent. It is proven to be an effective way in separating biomass solids from digester suspensions and recycle them to the digester.

However, in this membrane anaerobic system has to be monitored properly as the processes rely solely on the micro-organism to break down the pollutants. The micro-organism is very sensitive to changes in the environment thus great care have to be taken to maintain a conducive environment for the micro organism. Besides, there will be problem arises in the membrane system due to the characteristic of POME as it is a high suspended solids effluent. The membrane will be suffered from fouling and degradation during use. Thus, the objective of this study is to investigate optimum condition of the anaerobic digestion system as well as method to overcome the membrane fouling problem.

1.2 PROBLEM STATEMENTS

POME is a high strength wastewater. The direct discharge of Palm Mill Oil Effluent will cause severe environment pollution. Coming to the context of water and air pollution, POME is one of the agricultural wastes to blame on. Greenhouse gasses emitted from Palm Oil Mill Effluent anaerobic treatment pond such as methane and carbon dioxide exerted greenhouse effect to the earth. The capturing of methane gas will save the environment. Besides, the treatment of POME often incurs high non-profitable cost in an industry that reduces the company profit. In addition, the cost of fossil fuel increases with the increasing demand and the depleting resource making it even valuable. The concept of transforming waste to energy makes waste treatment seem more appealing and cost-effective.

1.3 OBJECTIVES OF THE STUDY

The research aims to solve the problem statements by accomplishing the following specific objectives:

a) To enhance the production of methane gas by providing a best condition.

b) To enhance the treatability of POME by Membrane anaerobic system.

c) To made an overall evaluation on Membrane Anaerobic System in treating POME.

1.4 SCOPE OF RESEARCH

In order to execute the objectives, a 150 L bioreactor system with ultrasonic will be designed in order to optimize the production of methane and overcome membrane fouling problem. The parameters such as pH and temperature are controlled and maintain in optimum operating condition. The production of methane gas in varying retention time is investigated. The system performances were evaluated with parameter such as Chemical Oxygen Demand, Biological Oxygen Demand, Total Suspended Solid, and Volatile Suspended Solid for the raw material, material in the reactor and the treated permeate to observe the efficiency of the system.

1.6 RATIONALE AND SIGNIFICANT

The study can contribute by providing an alternative renewable energy that can be apply in the industry in return overcome the dependency on fossil fuel which is incurs high cost. Besides, it can protect the environment by reducing the emission of green house gasses to the environment such as methane gas and carbon dioxide. Meanwhile, reducing cost for POME treatment. It is also a good opportunity to attract foreign investor.

CHAPTER 2

LITERATURE REVIEW

2.1 PALM OIL MILL EFFLUENT (POME)

POME is generated as a result of sterilization of fresh palm oil fruit bunches, clarification of palm oil and effluent from hydro cyclone operation. (Borja et al, 1996) POME is a high strength agro-industrial polluter due to high value of COD and BOD.POME is in a form of highly viscous dark brown colloidal with fine suspended solid. POME colloidal suspension of 95-96% water, 0.6-0.7% oil and 4.5% total solids (Ma, 1993). The characteristic of POME are shown in Table 2.1. In 1980, Malaysian mills discharged 6 million tonnes of effluent which contain equivalent BOD as load generated by population of 7.3 million. However it's highly amendable by anaerobic digestion.

Table 2.1: Characteristic of untreated POME

Parameter	Concentration
pH	4.7
Temperarture	80-90
BOD 3-day, 30˚C	25,000
COD	50,000
Total soilids	40,500

Suspended solids	18,000
Total volatile Solids	34,000
Ammoniacal-Nitrogen	35
Total Nitrogen	750

*All parameter in mg/l except pH and temperature (˚C)

Source: (A.L Ahmad, 2003)

2.2 KYOTO PROTOCOL AND GOVERNMENT POLICY

In 1997, the Kyoto Protocol was adopted, calling for stronger action in reducing Green House Gases or GHG emission in the post 2000. Under the protocol, developed countries have a legally binding commitment to reduce their collective emissions of six greenhouse gases by at least 5% based on the 1990 levels by the period 2008 to 2012. The Protocol also establishes an emission trading regime including clean development mechanism (CDM) to facilitate countries to fulfill their commitments. CDM allows developed nations to achieve part of their reduction obligations by buying emission reductions from projects that reduce greenhouse gas emissions in developing countries period. On 12th March 1999, Malaysia signed the Kyoto Protocol and ratified it on 4th September 2002. With the ratification of the Kyoto Protocol by the Malaysian Government, this implies that Malaysians can benefit from investments in the GHG emissions reductions. (Lim, C.H. et al, 2006)

The utilization of methane gas from Palm Oil Mill Effluent (POME) for electricity generation can be used to obtain certified emission reduction (CER) and to be credited by clean development mechanism (CDM). (Poh P.E et al, 2009) The project will also contribute positively to Malaysian Government sustainable development effort to supply Renewable Energy to the nation for electricity generation under Five-Fuel Policy. Five-Fuel Policy was introduced in 2001 under the 8th Malaysia Plan to augment the National Energy Policy was introduced in 1979. The aim was to guide the country’s energy mix towards five fuels namely oil, gas, coal, hydro and renewable energy. Due to the unfulfilled target, the effort is continued the Fifth-Fuel Policy to be continued into the 9th Malaysia Plan from 2006 to 2010. (Kementerian Tenaga, Air Dan Komunikasi, 2005)

2.3 METHANE GAS FOR ELECTRICITY GENERATION

The generation of electricity from methane is possible, in all cases the steps that must be gone through are twofold, chemical energy to mechanical energy, and then from mechanical energy to electrical energy. For these conversion processes to be achieved, suitable engine is needed, and in principle there are two types of engine which have been used for biogas digester electricity generation that is gas engine and steam turbine.

According to the Malaysia Palm Oil Board (MPOB), 0.65 m3 POME is generated from every processed ton of Fresh Fruit Bunch. Based on a study of the potential for electricity generation from POME that have done by MPOB, if there was 38,870,000 m3 of POME produced for every 59,800,000 tons of Fresh Fruit Bunches process annually. The annual energy content of the generated methane gas can be calculated to 7.07E+09 kWh. Based on a conversion efficiency of 38 percent (gas engine), the potential annual electrical power generation would be 2.69E+09 kWh. Thus, Palm Oil Mill Effluent has a huge potential for power generation (N.A Ludin et al, 2006).

2.4 POME TREATMENT

2.4.1 Ponding System/Lagoon system/Open Digester tank

Ponding system is the most common system employed in Malaysia which counted for 85% of the total treatment plant in Malaysia. In a ponding system it is basically divided into de-oiling pond tank, acidification ponds, anaerobic ponds and facultative pond or aerobic ponds. The discharge after the facultative or aerobic require further reduce of BOD to comply with the discharge standards. The typical size of the ponding system is equivalent to half a soccer field which is able to sustain the processing capacity of 54 tons per hour. This method is favored due to it can achieve reasonable degree of treatment with low construction and operating cost and is easily maintained as the technology employed is relatively unsophisticated. However, a large land space is required. Direct emission of gasses generated in the treatment process will impose green house effect to the environment. Besides, the effectiveness in meeting the stringent standard is unsatisfactory. (Poh P.E et al, 2009)

Open digester tank are used for POME treatment when limited land area is available for ponding system. Apart from that, in the investigation by Yacobs et al (2006), he proved that anaerobic system emitted higher amount of methane compare to the open digester tank with an average methane composition of 54.4% compare to open digester tank. (Poh P.E et al, 2009)

2.4.2 Anaerobic Digestion

A biochemical process by which organic matter is decomposed by bacteria in the absence of oxygen, producing methane and other by products. It's much depends on the bacterial consortia for degradation process, thus a longer time is require. The condition is also required to be always in the optimum condition for the bacterial to survive, as the bacterial are sensitive. However, anaerobic digestion is widely used to treat waste as it require low energy, high organic removal rate, low sludge production and production of methane as valuable by product. (Poh, P.E. et al, 2009)

The degrading process of POME consists of four stages that is hydrolysis and acidogenesis, fermentation, acetogenesis, methanogenesis (Poh, P.E et al,2009). In the first stage of hydrolysis, the polymeric organic materials are hydrolysed to its constituent such as glucose, fatty acids and amino acids by hydrolytic bacteria. The hydrolysis process is of significant importance in high organic waste and may become rate limiting. Solubilisation involves hydrolysis process where the complex organic matter is hydrolysed into soluble monomers. Fats are hydrolysed into fatty acids or glycerol; proteins are hydrolysed into amino acids or peptides while carbohydrates are hydrolysed into monosaccharides and disaccharides.

In fermentation stage, the hydrolysed products are converted to volatile fatty acids, alcohols, aldehydes, ketones, ammonia, carbon dioxide, water and hydrogen by the acid-forming bacteria. The organic acids formed are acetic acid, propionic acid, butyric acid and valeric acid. Volatile fatty acids with more than four-carbon chain could not be used directly by methanogens (Wang et al., 1999).

The following stage is acedogenesis, where organic acids are further oxidised to acetic acid and hydrogen and carbon dioxide which are used in the subsequent process. Acetogenesis also includes acetate production from hydrogen and carbon dioxide by acetogens and homoacetogens.The transition of the substrate causes the pH of the system to drop which beneficial to acidogenic and acetagenic.(K.M Ostrem et al,2004)

Finally the reaction come across the the stage of methanogenesis. One is conversion of acetate to carbon dioxide and methane by acetotrophic organisms and another is reduction of carbon dioxide with hydrogen by hydrogenotrophic organisms. (Ling,L.Y, 2007).

Typical reaction of anaerobic digestion:

$$C_6H_{12}O_6 \longrightarrow 2C_2H_5OH+CO_2 \quad [1]$$

$$C_2H_5OH+CO_2 \longrightarrow CH_4+ 2CHOOH \quad [2]$$

$$CH_3COOH \longrightarrow CH_4 + CO_2 \quad [3]$$

$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O \quad [4]$$

The advantages of adopting anaerobic system are low energy requirement as no aeration needed. Methane is produced as a valuable end product and generates sludge that could be used for land application. There are several anaerobic treatment method that have been widely used such as Anaerobic filtration, fluidized bed reactor, up-flow anaerobic sludge blanket reactor (UASB), Up flow anaerobic sludge fixed-film reactor (UASFF), continuos stirred tank reactor and Anaerobic contact process. Although these high rate or hybrid reactors are successfully shortened the retention time and efficiency (as shown in table) but all these biological treatment systems need proper maintenance and monitoring as the processes solely rely on micro-organisms to degrade the pollutants. How to ensure the stability of the system deserves most urgent concern. (Y.J Zhang et al, 2007) .The summary of comparisons of all other method are shown in table 2.2.

Table 2.2: Comparisons of various treatment methods on POME treatment

Performance of various anaerobic treatment methods on POME treatment

	OLR (kg COD/m^3day)	Hydraulic retention time (days)	Methane composition (%)	COD removal efficiency (%)	Reference
Anaerobic pond	1.4	40	54.4	97.8	Yacob et al. (2006a)
Anaerobic digester	2.16	20	36	80.7	Yacob et al. (2005)
Anaerobic filtration	4.5	15	63	94	Borja and Banks (1994b)
Fluidized bed	40.0	0.25	N/A	78	Borja and Banks (1995b)
UASB	10.63	4	54.2	98.4	Borja and Banks (1994c)
UASFF	11.58	3	71.9	97	Najafpour et al. (2006)
CSTR	3.33	18	62.5	80	Tong and Jaafar (2006)
Anaerobic contact process[a]	3.44	4.7	63	93.3	Ibrahim et al. (1984)

N/A: data unavailable.
[a] In terms of BOD.

Source: (Poh P.E et al, 2009)

2.4.3 Membrane Separation Technology

Membrane Separation technology is always employed in waste treatment as it's able to produce consistent and good water quality after treatment plants as well as it's able to disinfect the treated water. There have been inspiring performances by using membrane separation technology. For instances, A.L Ahmad et al (2003) have shown that the combination of UF & RO is able to achieve COD removal of 98.8%,BOD removal of 99.4%, Turbidity of 100% and pH 7 as a result. Another group of researcher have incorporated Hollow fiber membrane in their three phase decanter system to give

89.9% COD removal, 99.4% of TSS elimination, 97.9% Turbidity reduction and 92.9% for color removal (S.S Raja et al, 2005).However, short membrane life, membrane fouling and expensive cost are major constraint of this technique. In order to prolong the membrane life span and produce crystal clear effluent as well as methane as the end product, the integration of anaerobic system and membrane separation technology in a bio reactor is investigated by some researchers.

2.4.4 Membrane Anaerobic System

The idea of integration of the anaerobic digestion system and membrane separation technology is to enable the biomass to be retained in the reactor which improves methane gas emission as well as producing constant high quality effluent. According to Y.J Zhang et al in 2007 she has incorporating Expanded Granulated Sludge Blanket (EGSB) with UF & RO. As a result, COD Removal of 93%, biogas conversion rate of 43% is achieved. As we compared the result to the previous table, the biogas generation appears to improve drastically. In the later years, H.N Abdurahman et al (2011) have shown another more inspiring result by his Membrane Anaerobic System which a design of anaerobic bioreactor equipped with UF module membrane where COD Removal efficiency 96.6%-98.4% and biogas conversion rate up to 73% as a final result.

However, although the membrane fouling problem may relief compared to the case without anaerobic digestion as pretreatment but the membrane fouling problems still an issues and the idea of back flushing membrane which require an operation break is not feasible to the industrial application. Hence, as a solution application of ultrasonic technology in solving the membrane fouling problem is going to be investigated in this research work.

2.5 METHANOGENS

Methanogen are specialized group of Archae that utilized a limited number of substrates, principally acetate, carbon dioxide and hydrogen for methane production or methanogenesis. These substrate resulted from the degradation from more complex substrate. Methane-forming bacteria have many shapes (bacillus, coccus, and spirillum), sizes (0.1 to 15µm), and growth patterns (individual cells, filamentous chains, cubes, and sarcina). Methane-forming bacteria are oxygen-sensitive anaerobes and are found in habitats that are rich in degradable organic compounds. In these habitats oxygen is rapidly removed by bacterial degradation of the organic compounds.

Methane-forming bacteria are active within the pH range of 6.8 to 7.2. Methane forming bacteria are sensitive to pH values <6.8 and >7.2. With decreasing pH, methane-forming bacteria become less active, while fermentative bacteria remain active and continue to produce fatty acids. These acids destroy alkalinity and depress pH resulting in inhibition of methane-forming bacteria. Also, with decreasing pH, increases in the quantities of hydrogen sulphide (H2S) and hydrogen cyanide (HCN) occur. These two inorganic compounds are highly toxic to methane-forming bacteria. With increasing pH, an increase in the quantity of ammonia (NH3) occurs. Ammonia also is toxic to methane-forming bacteria. Therefore, anaerobic digesters should be operated at a near neutral pH value and should be monitored as needed to ensure an acceptable pH value and alkalinity residual.

Sufficient alkalinity is necessary for proper pH control. Alkalinity serves as a buffer that prevents rapid change in pH. Enzymatic activity of methane-forming bacteria is adversely affected by pH values <6.8 and >7.2. Adequate alkalinity in an anaerobic digester can be maintained by providing an acceptable volatile acid-to alkalinity ratio. The range of acceptable volatile acid-to-alkalinity ratios is 0.1 to 0.2.

Because methane-forming bacteria reproduce very slowly (generation times of 3–30 days) and produce very few offspring (sludge) from the degradation of substrates (approximately 0.02 pounds of sludge per pound of substrate degraded), methane-forming bacteria require smaller quantities of most nutrients. However, there are a few nutrients that are required by methane-forming bacteria in quantities two to five times greater than most other bacteria. These nutrients are cobalt, iron, nickel, and sulphur.

Methanogenesis occurs through three basic biochemical reactions that are mediated by three different groups of methane-forming bacteria (acteoclastic methanogens, hydrotrophic methanogens, and methyltrophic methanogens). Acetoclastic methanogens produce methane by "splitting' acetate as shown in reaction equation 5. Hydrogenotrophic methanogens produce methane by combining hydrogen and carbon dioxide [6] while methyltrophic methanogens produce methane by removing methyl (−CH3) groups from simple substrates. In anaerobic digesters, acetoclastic methane-forming bacteria produce most of the methane, while hydrotrophic methane-forming bacteria produce approximately 30% of all methane. Methyltrophic methane-forming bacteria produce a relatively small quantity of methane in anaerobic digesters.

$$CH_3COOH \text{------------>} CH_4 + CO_2 \qquad [5]$$

$$CO_2 + 4H_2 \text{--------------->} CH_4 + 2H_20 \qquad [6]$$

(Michael H. Geradi, 2006)

2.6 ANAEROBIC DIGESTION OPERATION

2.6.1 pH

pH is the crucial factor that determine whether the Membrane anaerobic system is working. The microbial community in anaerobic digester is sensitive to pH change. The pH affects the process in 2 ways that are affecting the enzymatic activity by changing their proteic structure which may occur drastically as a result of changes in the pH and affecting the toxicity of a number of compounds indirectly eg sulphide toxicity. The optimum pH for methane producing microorganism to achieve optimum growth range between 6.6 and 7.4 (V.S Marcos et al,2005). Methane producing bacteria require a neutral to slightly alkaline environment (pH 6.8 to 8.5) in order to produce methane

(D.A Burke et al, 2001). Acid forming bacteria grow much faster than methane forming bacteria. If acid-producing bacteria grow too fast, they may produce more acid than the methane forming bacteria can consume. Excess acid builds up in the system. The pH drops, and the system may become unbalanced, inhibiting the activity of methane forming bacteria. Methane production may stop entirely.

Besides, the methanogenesis is strongly affected by pH and will be inhibited by the acid condition. The optimum pH for the methanogenesis stage is pH between 7.2-8.2 .If the pH fall below the pH of 6, anaerobic degradation rate will decrease and the lipids are not degraded (Ling,L.Y., 2007).The Acetic and butyric acids are favourable substrate for methanogens which form under neutral and acidic condition.

In addition, sudden pH change (pH shock) can adversely affect the process, and recover depend on series of factors, related to the type of damage caused to the microorganism (either permanent or temporary). The buffer capacity used must be understood to avoid changes in pH (V.S Marcos et al, 2005).

2.6.2 Mechanical Mixing

Mixing will provides good contact between substrate and microbes ensure the temperature is uniform, reduce resistance to mass transfer, minimized build up of inhibitory intermediate and stabilizes environment conditions (N.H Abdurahman et al, 2010). The same theory is proposed by Leslie Grady et al (1999) as well where mixing able to bring bacteria consortia into contact with food. The agitation of the mixing will also reduce the particle size which promotes the release of biogas from mixing (Karim et al, 2005).

The bioreactor with stirrer have been applied by a mill under Keck Seng (Malaysia) Berhad in Masai Johor since 1980s.The palm oil mill successfully achieved 83% COD removal and production of 62.5% methane production (Poh P.E et al, 2009). In the research of Kim.M et al (2002), Mesophilic non-mixed reactor failed earlier than the continuously stirred reactors even though it showed much better performance than the continuously fed reactors prior to reactor failure when organic loading rate added up until reactor failure. (Kim.M et al, 2002).Besides, mechanical mixing is also exhibit a positive results in producing methane gas in the research of Choorit W. et al where a Mesophilic continuous stirred tank reactor is being used. Another inspiring example is research done by Ugoji (1997), the experiments display a result of COD removal in between 93.6 to 97.7% (Poh P.E, 2009). However, the complete mixed system is more sensitive to temperature changes (Kim M.et al, 2002).

In the animal waste research of Karim et al (2005) suggested that mixing improved the performance of digesters treating waste with higher concentration while slurry recirculation showed better results compared to impeller and biogas recirculation mixing mode. Mixing also improved gas production as compared to unmixed digesters. (Poh P.E, 2009) Boe K. et al have adopted intermittent mixing in the research of biogas production from manure rather than vigorous mixing (Boe K. et al, 2009). Research of Kaparaju et al. (2008) is also agreed with the theory of intermittent mixing advantageous over vigorous mixing. However, mixing during start up is not beneficial as the digester pH will be lowered resulting in performance instability as well as leading to a prolonged start-up period.(Poh P.E, 2009).However there are no systematic research on mixing in treatment of POME.

2.6.3 Organic Loading Rate

Organic Loading rate is a measure of the anaerobic digestion biological conversion capacity. Various studies have proven that Organic Loading Rate (OLR) will reduce COD removal efficiency. However, it give a positive impact on the gas production where increase of with OLR until a stage when methanogens could not work quick enough to convert acetic acid to methane which in return increased the hydrogen partial pressure concomitantly decreased the methane yield. (N.H Abdurahman et al, 2010), (H.Patel et al,2002).

2.6.4 Temperature

The temperature range for anaerobic digestion can be categorised into Psychrophilic (<25˚C), Mesophilic (25 to 40˚C) and thermophilic (<45˚C).Methane production have been documented in various range of temperature, but the most productive in either mesophilic conditions, at 30-35˚C or in the thermophilic range at 50-55˚C.Once the maximum specific growth rate of microbial population rises as the temperature increase. However, maintaining a uniform temperature in the reactor maybe more important, once the anaerobic process is considered very sensitive to abrupt temperature changes, which may cause unbalance between the two largest microbial population and consequently result in process failure (the usual limit is about 2 ˚C per day) (V.S Marcos et al, 2005).

In mesophilic temperature condition methane forming micro-organism range belong to the genera *Mathanobacterium, Methanobrevibacter* and *Methanospirillum*, which are hydrogen-using micro-organism and to the genera Methanosarcina and Methnosaeta which are organism that use acetate to form methane. The temperature affects the biological enzymatic reaction rate and influencing substrate diffusion rate. (V.S Marcos et al, 2005).There are several research successfully produce methane in Mesophilic temperature such as K.M Ostrem et al proved that for the mesophilic digester to operate to the optimum, the temperature have to be maintained at 30-35˚C(K.M. Ostrem et al,2004). Besides, N.H Abdurahman et al conducted their experiment in the Mesophilic temperature range and shown positive result in the production of methane (N.H Abdurahman, 2010). In the research of Zhang Y.J et al has once again shown that Mesophilic temperature range favour the production of methane (Zhang Y.J et al, 2007).

As mentioned before, methane production is productive in thermophilic condition as well. However, for a thermophilic digester the start up period is much longer than mesophilic digester to allow mesophilic sludge to acclimatize with the substrate as well as temperature swift (Poh P.E et al, 2010). There are several attempts to overcome this problem such as by introducing seed sludge for cultivation of mixed culture but it takes a longer time and even more expertise (eg. Molecular biology to identify the microbes in mixed cultured) to get the digester works well. (Poh P.E et al, 2010) Hence, the operational experience in this temperature range not been satisfactory and still many pending question such as whether resulting benefits overcome disadvantage, including additional energy required which increase operational cost, the poor quality supernatant and instability of the process. Besides, the external effects of the temperature on bacterial cell are important. For example, the degree of dissociation of several compound depend strongly on temperature such as specific case of ammonia. The thermodynamic of several reactions are also affected such as the dependence of the hydrogen pressure in anaerobic digesters where fermentation occurs in appropriate manner (V.S Marcos et al, 2005). B.K. Ahring et al (1995) shown that the perturbation of temperature impose the greatest effect on the final product of the such as methane production. Methane production almost ceased after the increase of temperature and had not resumed even 10 days later indicating the importance of a stable temperature of the process.

In the later year, the temperature phase anaerobic digester (TPAD) is developed in with combination of mesophilic and thermophilic condition, the two stage digester show improvement in performance. More than 20 full scaled TPAD systems have been set up in United State for wastewater treatment (S.Sung, 2003). Despite of the advantages of the system, some researchers would go for other options as there are disadvantages in separating the acidogenic and methanogenic reaction which in turn disrupt the synthrophic relationship between bacteria and methanogens in addition of the complicated control process (Boe K et al, 2009).

As a result, Mesophilic digester would be chosen as the digester in this experiment to produce methane in a steady performance with the minimum constraint.

2.6.5 Hydraulic Retention time

Hydraulic Retention Time (HRT) is the number of days the materials stays in the tank. The Hydraulic Retention Time equals the volume of the tank divided by the daily flow (HRT=V/Q). The hydraulic retention time is important since it establishes the quantity of time available for bacterial growth especially for the growth of hydrolytic acidogenic bacteria and subsequent conversion of the organic material to gas (D.ABurke., 2001) The HRT is closely related to the OLR and substrate concentration, thus a good balance have to be achieve for good digester operation. (N.H Abdurahman, 2010).

2.6.6 Solid Retention time

The Solids Retention Time (SRT) is the average time the activated-sludge solids are in the system. The SRT is an important design and operating parameter for the activated-sludge process and is usually expressed in days. (Lenntech, 2010) Although the calculation of the solids retention time is often improperly stated, it is the quantity of solids maintained in the digester divided by the quantity of solids wasted each day as shown in equation below:

$$SRT = \frac{(V)(Cd)}{(Qw)(Cw)} \quad [7]$$

V = Digester Volume

Cd = Solid Concentration in the digester

Cw = Solid Concentration in the waste

Qw = Volume wasted each day

In a conventional completely mixed, or plug flow digester, the HRT equals the SRT. However, in a variety of retained biomass reactors the SRT exceeds the HRT. (D.A Burke, 2001) As a result, the retained biomass digesters can be much smaller while achieving the same solids conversion to gas. At a low SRT sufficient time is not available for the bacteria to grow and replace the bacteria lost in the effluent. If the rate of bacterial loss exceeds the rate of bacteria growth, "wash-out" occurs. The SRT at which “wash-out” begins to occur is the "critical SRT". (M. Clara et al, 2004).

2.6.7 Volatile Fatty Acid

Volatile Fatty acid had been use as the process balance indicator. Change in VFA level were shown to be a good parameter, under unstable operation, intermediate such as volatile acid and alcohol accumulates at different rate depending on the substrate and type of perturbation causing instability. The volatile fatty acid accumulation reflects a kinetics uncoupling between acid producers and consumers and is typical for stress situations. (B.K Ahring et al, 1995) Review back to the fermentation stage the acidogenic bacteria convert the less soluble organic compounds to organic acids such as acetic acid, propionic acid and butyric acid which known as volatile fatty acids, alcohol and other intermediates. (Husnul Azan T. et al, 2006) Hence, accumulation of VFA indicates that the further digestion into methanogenic stage is affected. Besides, the imbalance can be reflected by pH, volatile solid reduction and gas composition. However, these are often too slow for the optimal detection of sudden changes. The VFA concentration results in pH drop in turn causing toxicity to the system. pH changes are small in highly buffered systems as often seen in reactor with high ammonia loads even when the process is severely stressed. Hill et al (1987) suggested that acetate concentration higher than 13mM have been suggested to indicate imbalance. Hill (1982) proposed that the propionate/acetate ratio should be used as a process indicator and a stable process should be below 1.4. In the later year on 1988, Hill and Holmberg showed that isobutyrate or isovalerate below 0.06 indicate stable process however different system have their own normal level VFA. (B.K Ahring et al,1995) Several studies shown that high concentration of VFA have no effect on the biogas process.

2.7 MEMBRANE TECHNOLOGY

Advance treatment process such as membrane separation shows accelerated market growth result by the stringent environmental legislation and water scarcity around the world. Application of membrane technology which commonly employed in waste water treatment can contribute to developing an efficient waste water treatment process to produce high quality effluent and retain the biomass concentration within the reactor at the same time.

In general there are 5 types of membrane filtration process that are conventional filtration, microfiltration, ultra filtration, nanofiltration and reverse osmosis. The selection type of membrane process depends on the particles size that requires separation. Table 2.3 shows the filtration processes with their properties and applications. On the other hand, table 2.4 shows the apparent dimension of some particles.

Table 2.3: Filtration process with their properties and applications

Filtration Process	Pore size	Seperation capability	Pressure (bar)	Application examples
NF	1-10nm	Mw200-20,000	5-25	Purification of sugar and salts,water treatment
UF	5-100nm	Mw of 10K-500k	0.5-5	Pharmaceutical industry, waste water treatment
MF	50nm-5µm	Bacteria and colloids	0.5-3	Prefiltration in water treatment, sterile filtratio

(Source: Ramakrishna et al, 2011)

Table 2.4: Apparent Dimensions of various Particles

Particle	**Dimension (µm)**
Yeast's, Fungi	1-10
Bacteria	0.3-10
Viruses	0.03-0.3
Protein ($10^4 - 10^6$ molwt)	0.002-0.1
Enzymes	0.002-0.005
Antibiotics , Polypeptides	0.0006-0.0012
Sugars	0.0008-0.001
Water	0.0002

Source : (N.H Abdurahman et al, 2011)

Membrane characteristics are relied on the geometry, flow direction, the surface characteristics (normally denoted by pore size) and materials which determining its properties such as the surface charges, hydrophobicity and porosity.

Pore size is the main physical properties determine its application for various feed solution characteristic. Ultra filtration membrane manufacturer frequently characterize their membranes using the "cut off" concept rather than pore size. The nominal molecular cut off weight defined as the lower limit of a solute molecular weight for which rejection is 95%-98%. As the molecular weight reduce the mean pore diameter for most UF is decreased. Hence, MWCO is a rough indication of the membrane ability to remove a given compound despite of other factor. (Norman N.Li, 2008) .

Besides, the materials of the membrane have great influence on performance. Synthetic polymer can be dividing into two classes that is hydrophobic and hydrophilic. Polysulfone ans polyethersulfone is hydrophilic and use for UF process. Hydrophobic membranes such as polytetraflouroethylene, polyvinylidene fluoride, polyethene are commonly used for MF. The fouling potential for the hydrophobic membrane is highly due to the high binding affinity of the proteins and humic substances.

Besides, the surface charges implies different fouling tendency. Generally, membrane materials carry a negative charge because natural organic matter is negative charge at neutral pH due to phenolic and carboxylic functional groups. A negative charge of membrane therefore prevent deposition of foulant by charge repel.

2.7.1 Hollow fiber membrane

The hollow fiber configuration is the most common configuration for MF and UF membrane. The hollow fibers are 05-1.0mm (less than 5mm) in diameter and several thousand of hollow fibers are packed in a module. The most important merits is that no extensive pretreatment needed as the membrane can be backwashed. The excellent mass-transfer properties conferred by the hollow fibre configuration soon led to numerous commercial applications in various field. The hollow fibre membranes have two major advantages over flat sheet membranes. One is that hollow fibres have much larger ratio of membrane area to unit volume, and hence higher productivity per unit volume of membrane module. Another is that they are self-supporting which can be back-flashed for liquid separation. (Cheresources, 2010).

Hollow fibre membrane can be operated in two different flow modes which are shell side feed and bore side feed. The bore side feed has its advantages over shell side feed including minimal pressure drop inside the fibers. The diameter is usually larger than those of the fine fibres used in shell side feed system, it is important to ensure all fibres have identical fibres diameters and permeance to ensure module performance. Feed pressure is usually limited below 150 psig.

UF system are operate in two possible filtration modes which is cross flow configuration in which the feed water is pumped tangential to the membrane while the water that does not permeate is recirculation as concentrate and combine with feed. In dead end or direct filtration all the feed water passes through the membrane. Therefore recovery is 100% and small fraction is used periodically for back wash. Although dead end filtration require lower energy but the cross flow filtration suit the system better where recirculation of retentate is encouraging.

2.8 MEMBRANE FOULING

A major obstacle for the application of Hollow fibre membrane in MAS is the rapid decline of the permeation flux as a result of membrane fouling (Cheresources, 2010). Fouling refers to blockage of membranes pores during filtration caused by the combination of sieving and adsorption particulates onto membrane surface and within the membrane pore. This blockage of the pores causes a flux decline over time when all other parameter kept constant. The predominant fouling mechanisms observed with ultrafiltration and micro filtration membranes are classified into three categories: the build-up of a cake layer on the membrane surface, blocking of membrane pores, and adsorption of fouling material on the membrane surface or in the pore walls (M.O.Laminen, 2004). To establish strategies for fouling control, understanding of the fouling mechanisms is indispensable. Sludge characteristics are significant parameters that affect membrane fouling in MAS.

Fouling can be broadly classified into backwashable and irreversible. Backwash able can be removed either by backwashing or chemical cleaning while the irreversible type neither of the method can recover the original flux.

Fouling can also be classified according to type of the fouling materials. Four categories of the membrane fouling are generally reognised. They are:

a) Inorganic fouling
b) Particle /colloidal fouling
c) Microbial fouling
d) Organic fouling